Mo/W containing peptides as novel catalysts for CO_2 valorization

Context

The recycling of CO_2 has become an essential challenge for our societies as it remains impossible to avoid completely the production of this greenhouse gas. Transforming CO_2 into value-added products would offer a plausible solution to this societal need. In this regard, chemists have devoted plenty of efforts to develop catalytic processes for CO_2 valorization. With this in mind, our group got interested in formate deshydrogenases (FDHs), Molybdenum (Mo) and Tungsten (W)-containing enzymes capable of catalyzing the reversible conversion of formate to carbon dioxide ($HCOO^- = CO_2 + H^+ + 2e^-$). These enzymes have their Mo/W atom coordinated by two pyranopterin-dithiolene ligands conjugated to guanine dinucleotide leading to a Mo/W-bisPGD cofactor (Moco) [2]. The coordination sphere of the metal is completed by a cysteine- or selenocysteine in the fifth position, and sulfur atom in the sixth position. FDHs have thus become a source of inspiration for the development of new catalysts for CO_2 valorization.

PhD Project

In this project, we intend to develop bio-inspired FDHs Mo/W-peptidic systems with the final goal of obtaining efficient molecular catalysts for CO_2 reduction. Different peptidic scaffolds that will contain non-natural dithiolene-like amino acids to coordinate Mo and/or W will be designed and synthesized following established protocols [3]. The Mo/W-peptides complexes will be characterized using different spectroscopic techniques (UV-Vis, Fluorescence, EPR, NMR, IR). Electrochemistry methodologies (cyclic voltammetry, bulk electrolysis) will be employed to identify the accessible redox states of the Mo/W-peptides complexes. Ultimately, their CO_2 reduction catalytic properties will be explored. Theoretical calculations will be conducted to rationalize and validate the experimental data (electronic structures, spectroscopic parameters and reactivity) in order to get a deeper understanding of the reactivities as well as a predictive tool to assist in the design of more effective catalysts.

References

1. a) R. Hille *et al.*, *Chem. Rev.*, 2014, 114, 3963; b) R. Hille, *Protein Science*, 2018, 28, 111.
2. S. Grimaldi at *al.*, *Biochim. Biophys. Acta*, 2013, 1827, 1048.
3. a) A. Fragoso *et al.*, *Chem. Eur. J.*, 2015, 21, 13100; b) A. Fragoso *et al.*, *Chem. Eur. J.*, 2013, 19, 2076.

Keywords

peptide chemistry, coordination chemistry, electrocatalysis, quantum chemistry, bioinspired complex, energy, CO_2 valorization

Required skills

Background in peptide synthesis and/or coordination chemistry.
Knowledge in electrochemistry, spectroscopy and quantum chemistry would be appreciated.

Applications

Candidates should send a CV, a motivation letter, transcripts of marks for the Master degree and contact of two referees to:

Dr Olga Iranzo olga.iranzo@univ-amu.fr & Dr Maylis Orio maylis.orio@univ-amu.fr
Aix Marseille University, iSm2 CNRS UMR 7313, BiosCiences team

Application deadline: **15/05/2020**